(21) 0.001–3 *m* HCl at 25 °C: H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions", 2nd ed, Reinhold, New York, N.Y., 1950, p 340. 3–16 *m* HCl at 25 °C: M. Randall and L. E. Young, *J. Am. Chem. Soc.*, **50**, 989 (1928).
(22) Mean activity coefficients for 0.1–4 *m* NaCl at 25 °C from H. S. Harned and L. F. Nims, *J. Am. Chem. Soc.*, **55**, 4855 (1933). Value for 4.95 *m* NaCl (expt 6, Table I) obtained by extrapolation of these values.
(23) β_2 and β_3 have been determined to be on the order of about 10^5–10^6 by a number of investigators. See ref 18.

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Simple Alkyne Adducts of $MoO(S_2CNR_2)_2$

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It has recently been shown that $MoO(S_2CNEt_2)_2$ can reversibly bind acetylene in solution whereas no binding between the complex and ethylene was observed.[1] Spectroscopic evidence demonstrated that the alkyne is bound cis to the oxo group and is in the plane which is perpendicular to the MoO bond vector. This geometry, which is readily predicted using simple bonding arguments, is identical with those found with the structurally characterized adducts of the activated alkene tetracyanoethylene[2] and the activated alkyne ditoluoylacetylene.[3] The actual isolation of acetylenic adducts has been accomplished up to this time in only those cases where the alkyne bears strongly activating substituents as in $RC\equiv CR'$ ($R = R' = CH_3C_6H_4CO$[3] or CH_3CO_2[4] and $R = CH_3CO_2$, $R' = H$[5]). We now wish to report the isolation and characterization of several adducts of $MoO(S_2CNMe_2)_2$ and $MoO(S_2CNEt_2)_2$ with the simpler alkynes acetylene, phenylacetylene, and diphenylacetylene.

Experimental Section

All manipulations were performed either under vacuum or in an argon atmosphere. Anhydrous, air-free CH_2Cl_2 was obtained by equilibration over P_2O_5 followed by distillation under vacuum. The oxomolybdenum(IV) complexes were prepared by a published procedure.[6] All other materials were reagent grade. Elemental analyses were obtained from Galbraith Laboratories. Infrared spectra were obtained using a Perkin-Elmer Model 283 spectrophotometer while ^1H NMR spectra were determined at 220, 100, and 60 MHz using Varian HR-220, XL-100, and T-60 spectrometers, respectively.

The alkyne complexes were prepared according to the following general procedure. The addition of 5 mmol of the alkyne to 25 mL of CH_2Cl_2 containing 0.6 mmol of either $MoO(S_2CNEt_2)_2$ or $MoO(S_2CNMe_2)_2$ rapidly discharged the initial rose color and caused the appearance of a bright orange-yellow color. The reaction is virtually heterogeneous when $MoO(S_2CNMe_2)_2$ is used but it is homogeneous when $MoO(S_2CNEt_2)$ is employed. For the latter, concentration followed by slow introduction of hexane by distillation causes the deposition of bright yellow crystals which can be removed by filtration. With the exception of the compound formed with diphenylacetylene, the analytical results shown in Table I are in accord with the formulation $MoO(alkyne)(S_2CNR_2)_2$. With diphenylacetylene, however, the product is $MoO(PhC_2Ph)(S_2CNEt_2)_2\cdot{}^1/_2PhC\equiv CPh$. The additional alkyne in this compound is undoubtedly a guest in the lattice since it was easily removed by either washing with hexane or extensive exposure to a dynamic vacuum.

The preparation of $MoO(HC_2H)(S_2CNMe_2)_2$ followed the same general procedure and again the reaction was virtually heterogeneous. However, the isolated product had sufficient solubility in CD_2Cl_2 to observe the major features of the ^1H NMR spectrum including the signal due to the bound acetylene. Furthermore, the infrared spectrum of the compound, when taken immediately after its isolation, only contained bands which could be ascribed to the adduct. However, the intensities of these bands slowly diminished while new bands due to $Mo_2O_4(S_2CNMe_2)_2$ appeared. The appearance of the dinuclear complex is due to a reaction with O_2 since the adduct is completely converted to $Mo_2O_4(S_2CNMe_2)_2$ on exposure to air. We assume that the other product is $H_2C{=}CH(S_2CNMe_2)$ since others[5] have observed that the reaction of $MoO(RC_2R')(S_2CNMe_2)_2$ ($R = R' = CF_3$; $R = H$, $R' = CH_3CO_2$) with O_2 from moist air results in the near-quantitative formation of the dinuclear compound and the corresponding alkene addition product. Although we took extreme precautions in preparing a sample of the alkyne adduct for commercial analyses, the analytical results which were returned to us point to decomposition of the adduct and virtually complete formation of the dinucear compound and the alkene in a mole ratio of 1:2. Anal. Calcd: C, 24.3; H, 3.83; N, 7.09; S, 32.5. Found: C, 23.9; H, 3.52; N, 7.18; S, 32.5.

Results and Discussion

Pertinent infrared and ^1H NMR data are included in Table II. Coordination of the alkyne results in a decrease in the MoO stretching frequencies by about 30 cm^{-1} from the values observed with the parent oxomolybdenum(IV) complexes. Similarly, coordination of the alkyne causes a decrease in the carbon–carbon stretching frequency of about 300 cm^{-1}. The NMR spectra of those complexes in which the bound alkyne possesses acetylenic hydrogen atoms revealed considerable deshielding of these atoms as evidenced by their downfield shifts of about 6 ppm relative to the values observed with free alkyne. These observations lend further credence to the suggestion that the formation of these complexes[3] as well as those of the azodicarboxylates[4] involves a formal two-electron oxidative addition of the alkyne to the oxomolybdenum(IV) species. Simple bonding arguments suggest that the bond order of the MoO bond in the latter should be three since the empty d_{xz} and d_{yz} orbitals of the metal can overlap with the filled $p\pi$ orbitals of the oxo ligand. Housing two electrons in the d_{xy} orbital then accounts for the diamagnetism. The bond order of the MoO fragment is then maintained if the alkyne occupies the *xy* plane. The filled d_{xy} orbital can overlap effectively with an empty π^* orbital of the alkyne resulting in a transfer of electron density from the metal to the alkyne. The resulting complex can be described as a pentagonal bipyramid in which the equatorial sites are occupied by the carbon atoms of the alkyne and three sulfur atoms from two bidentate ligands.

Spectroscopic techniques have allowed us to demonstrate that the dynamic equilibrium shown in eq 1 exists when those

$$MoOL_2 + \text{alkyne} = MoO(\text{alkyne})L_2 \qquad (1)$$
$$L = S_2CNEt_2$$

complexes having appreciable solubility are dissolved in CH_2Cl_2. Both bound and dissociated species are observed using NMR spectroscopy as well as infrared spectroscopy[1] even at ambient temperature. The addition of excess alkyne or a decrease in the temperature will cause the equilibrium to shift in favor of the adduct. The spectrum of $MoO(HC_2H)(S_2CNEt_2)_2$ at −55 °C, 100 MHz, and a 25-fold excess of acetylene is shown in Figure 1. Two signals due to the methyl hydrogen atoms of the ligands appear in a 3:1 distribution. A similar distribution can also be observed for the two signals caused by the methylene hydrogen atoms. We have observed a similar pattern in the spectrum of $MoO(PhC_2Ph)(S_2CNEt_2)_2$. This region of the spectrum of $MoO(PhC_2H)(S_2CNEt_2)_2$, however, is complicated somewhat by overlapping resonances due to two possible orientations of the alkyne. Additional comments about the consequences of these orientations appear later in this paragraph. The spectrum of $MoO(RC_2R)(S_2CNEt_2)_2$ ($R = CH_3CO_2$), a compound which does not dissociate appreciably according to eq 1, shows only the simple 3:1 patterns at ambient temperature. The stronger binding of this alkyne is caused by more extensive electron withdrawal ($d_{xy} \rightarrow \pi^*$) demanded by the carboxylate groups. The qualitative similarity of these features in the NMR spectra

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Table I. Analytical Results

complex	calcd %C	calcd %H	calcd %N	calcd %S	found %C	found %H	found %N	found %S
$MoO(PhC_2Ph)(S_2CNEt_2)_2\cdot{}^1/_2PhC_2Ph$	55.1	5.22	4.14		55.0	5.17	4.21	
$MoO(PhC_2Ph)(S_2CNEt_2)_2$	49.1	5.15	4.77	21.9	48.9	5.17	4.73	21.9
$MoO(PhC_2Ph)(S_2CNMe_2)_2$	45.3	4.18	5.28		45.0	4.24	5.20	
$MoO(PhC_2H)(S_2CNEt_2)_2$	42.3	5.13	5.48	25.1	42.1	5.18	5.33	25.3

Table II. Spectroscopic Data and Equilibrium Quotients[a]

complex	ν(MoO),[b] cm^{-1}	ν(C≡C),[b,c] cm^{-1}	δ(≡C–H),[c–e] ppm	K_{eq},[e] M^{-1}
$MoO(PhC_2Ph)(S_2CNEt_2)_2$	935	1820		25
$MoO(PhC_2Ph)(S_2CNMe_2)_2$	926	1824		
$MoO(PhC_2H)(S_2CNEt_2)_2$	930	1780 (2105)	8.80 (3.05)	22
$MoO(HC_2H)(S_2CNEt_2)_2$[f]	935	1684 (1974)	8.73 (2.04)	20
$MoO(HC_2H)(S_2CNMe_2)_2$	930	1665 (1974)	8.68 (2.04)	

[a] For eq 1 in the text. [b] All infrared spectra were obtained in Nujol mulls except where noted. [c] Parenthetic values are for the free alkyne. [d] Chemical shifts are downfield from the signal due to Me_4Si. [e] Measured at 21 °C in CD_2Cl_2. [f] Data taken from ref 1. The infrared spectra were measured in CH_2Cl_2.

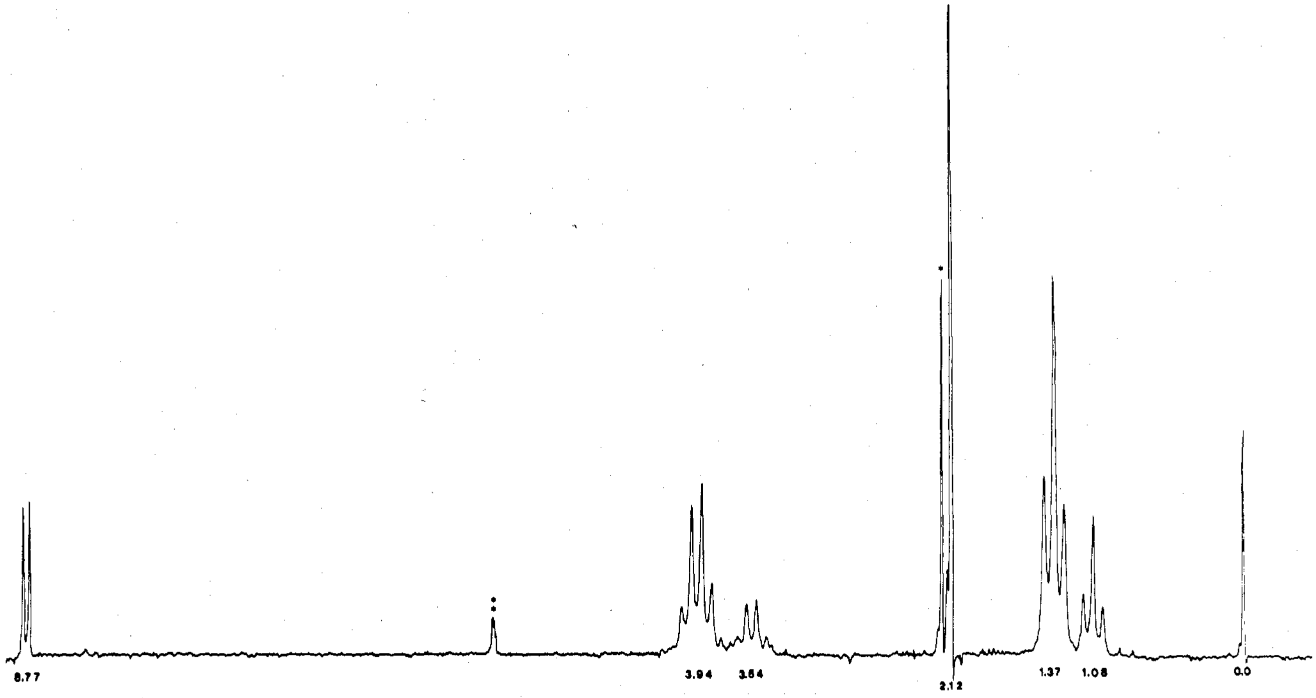

Figure 1. The ^1H NMR spectrum of $MoO(HC_2H)(S_2CNEt_2)_2$ in CD_2Cl_2 at 100 MHz and −55 °C. Free and bound acetylene appear at 2.12 and 8.77 ppm, respectively. The spectrum also contains a signal due to acetone (*) which is present as a stabilizer in commercially available acetylene and a signal from the protic forms of the solvent (**). Chemical shifts are measured with respect to Me_4Si.

undoubtedly indicate that all of the adducts are isostructural. Since these patterns are also observed at 220 MHz, the signals of higher intensity must result from a fortuitous degeneracy of the ethyl groups which more or less occupy the pentagonal plane perpendicular to the MoO bond vector. The weaker signals must then be due to the remaining ethyl group. The hydrogen atoms of bound acetylene are not expected to be equivalent in the predicted structure of the molecule and, indeed, two signals of equal intensity ($\Delta\nu$ = 7 Hz) resulting from these atoms are readily observed at low temperature as shown in Figure 1. Since only a single resonance is present at ambient temperature, it would appear that the bound alkyne is spinning rapidly at the higher temperature. The assumed geometry of the adduct will also allow two orientations of phenylacetylene. In confirmation, the spectrum of $MoO(PhC_2H)(S_2CNEt_2)_2$ at −50 °C contains two resonances at 9.00 and 9.11 ppm ($\Delta\nu$ = 11 Hz) due to the two orientations of the ethynyl hydrogen atom. Since the intensities of these signals are roughly equivalent, we must assume that both orientations have a near-equal probability. This assumption is not unreasonable since binding of the alkyne is expected to cause the phenyl group and the hydrogen atom to bend away from the metal as is observed with the two phenyl groups of $Pt(PhC_2Ph)(Ph_3P)_2$.[7] Consequently, steric interactions between these groups and the remainder of the complex will be decreased.

The equilibrium quotient for the reaction in eq 1 at 21 °C has been obtained, in each case where solubility permitted, by estimating the relative intensities of the partially overlapped NMR signals due to the methyl and methylene hydrogen atoms of $MoO(S_2CNEt_2)_2$ and the alkyne adduct. The results are given in Table II. An additional means to calculate the equilibrium quotients is provided by the drastic differences in chemical shifts of the signals due to the ethynyl hydrogen atoms of bound and free acetylene and phenylacetylene. The values obtained by this method and those obtained by the first method agreed to within 10%. Unfortunately, the resonances due to the phenyl hydrogen atoms are not appreciably shifted upon coordination and cannot be used to estimate an equilibrium quotient. A slight trend toward higher values of the equilibrium quotient seems to occur as phenyl groups are substituted for the hydrogen atoms of acetylene. While this trend could be easily rationalized, the small changes which are observed are only slightly above the estimated errors in the measurements.

The addition of gaseous HCl to solutions containing the alkyne adducts did not result in detectable amounts of alkenes. However, when $NaBH_4$ (5 mmol) was added to 5 mL of a THF–H_2O (4:1) solution containing $MoO(S_2CNEt_2)_2$ (0.6 mmol) and diphenylacetylene (0.6 mmol), complete reduction of the alkyne was achieved after 3 days at ambient temperature. This reduction yielded approximately equimolar amounts of cis and trans stilbenes as shown by NMR spectroscopy. A similar reaction with acetylene was previously demonstrated[1] although some butadiene was also detected in that reaction. Furthermore, neither of the stilbenes will bind detectably to $MoO(S_2CNEt_2)_2$ in agreement with our previous results with ethylene.[1] While these complexes are capable of binding alkynes, these results make it clear that they are not capable of spontaneous reduction of the alkyne in the presence of a proton donor. In contrast, another oxomolybdenum(IV) complex, *trans*-$MoO(H_2O)(CN)_4^{2-}$, will reduce acetylene to ethylene in water.[8]

It is also noteworthy that, unlike all other complexes described herein, the product from the reaction of $MoO(S_2CNMe_2)_2$ and acetylene is particularly susceptible to reaction with adventitious O_2. We have shown that one of the products of this reaction is $Mo_2O_4(S_2CNMe_2)_2$. Others have observed[5] that the reaction of $MoO(RC_2R')(S_2CNMe_2)_2$ (R = R' = CF_3; R = H, R' = CH_3CO_2) with moist O_2 results in the formation of the dinuclear compound and *trans*-$RCH{=}CH(S_2CNMe_2)_2$. We presume that the reaction of our complex proceeds by the same pathway but we have not actually detected the alkene. Although commercial analyses indicated extensive, if not complete, oxidation had occurred by the time of analysis, ^1H NMR and infrared spectroscopy (Table II) have provided good evidence that the alkyne adduct is the precursor to these oxidation products.

Since oxomolybdenum(IV) is capable of binding simple alkynes, but not the corresponding alkenes, there is an obvious analogy with the action of nitrogenase with acetylene.[9] An unusual feature in our observations, however, is that a metal with a high formal oxidation state is capable of binding an alkyne to a significant degree. The explanation probably lies with an input of a significant quantity of electron density by way of π bonding from the oxo ligand as well as the sulfur donor atoms. As a result, the actual oxidation level is considerably less than would result if only σ bonding were present. It may be that similar, but not necessarily identical, π bonding in nitrogenase allows the metal to cycle between formal oxidation states which are relatively high[10] while still retaining the ability to bind relatively soft substrates to a significant degree. Similar ideas have been advanced previously.[11]

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Registry No. $MoO(PhC_2Ph)(S_2CNEt_2)_2$, 68525-25-7; $MoO(PhC_2Ph)(S_2CNMe_2)_2$, 68525-26-8; $MoO(PhC_2H)(S_2CNEt_2)_2$, 68525-27-9; $MoO(HC_2H)(S_2CNMe_2)_2$, 68525-28-0; $MoO(HC_2H)(S_2CNEt_2)_2$, 66060-13-7; $MoO(S_2CNEt_2)_2$, 25395-92-0; $MoO(S_2CNMe_2)_2$, 39587-09-2.

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Synthesis, Characterization, and Magnetic Properties of Two Iron(III) Triketonates

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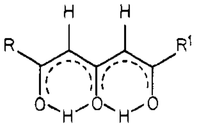
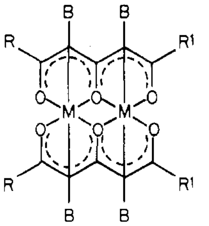
The function of the iron atom in biological processes is very important; consequently various model systems have been prepared for study. Certain biologically important enzymes contain polynuclear complexes of iron. For example, complexes containing Fe–O–Fe and Fe–N–Fe linkages are common in such biological processes as oxidation–reduction reactions.[1,2] Of utmost importance are the Fe–S–Fe linkages which are the backbone of the iron–sulfur proteins. Analogues of the latter have been studied extensively in the past few years, particularly by Holm and co-workers.[3]

The ligand system chosen for this study is that of the dianionic triketone.



R, R' = C_6H_5, CH_3
1,3,5-triketone



M = Co(II), Cu(II), Ni(II), $V^{IV}O$
B = Py, H_2O
1,3,5-triketonates

This ligand forms binuclear complexes with metal(II) ions of the first-row transition series as shown. These binuclear metal complexes allow the study of the interaction between transition-metal ions in finite surroundings because the ions in the cluster interact strongly with each other and the interaction between molecules can be neglected. Several binuclear complexes with a variety of metal ions have been prepared and